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13. ABSTRACT (Maximum 200 words)  Experimental studies and modeling of atomic bonding have been carried out for amorphous covalent alloys and CVD diamond films. The following results have been obtained: 1. Two distinct growth regimes have been found for CVD diamond films: an initial period of rapidly increasing roughness, followed by a slower increase as the diamond film grows further. 2. The difficulty in incorporating more than 10 at % N in PECVD a-C <sub>x</sub> N <sub>y</sub> H <sub>z</sub> films is related to plasma etching of the films. 3. Predictions for bonding in low ε alloys: Si-O and Si-F bonds are preferred in a-SiO <sub>2</sub> :F while Si-O, Si-F, and O-H bonds are preferred in a-SiO <sub>2</sub> :F:H. 4. A procedure has been developed for determining the optical constants and the volume fraction of the non-diamond carbon component of CVD diamond films. 5. Entropy have been found to play a critical role in determining the atomic bonding in diamond-like carbon alloys. 6. Phase separation is predicted to occur in a-Si <sub>x</sub> C <sub>y</sub> Ge <sub>z</sub> alloys due to the preference for Si-C and Ge-Ge bonds.				
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Final Report  
(for 9/1/96 - 8/14/97)

Studies of Electronic and Optical Materials:  
A. Interactions of Oxygen with Si-Ge Alloys and  
B. Deposition of Films for Optical Storage Applications

AFOSR Grant No. F 49620-94-1-0248

submitted by:

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### Objectives:

The objectives of the work to be carried out during the third and final year (plus four months extension) of AFOSR support (4/15/97 - 8/14/97) are as follows:

1. continuation of the studies of the deposition and characterization of amorphous BN:C alloy films.
2. completion of the studies of the initial growth phase of CVD diamond films.
3. establishment of an experimental facility for the measurement of the thermal conductivity of thin films of semiconductors and insulators.

### Status of Research Effort:

1. continuation of the studies of the deposition and characterization of amorphous BN:C alloy films.

Quasi-binary alloys of the general composition  $(\text{BN})_{1-x}\text{C}_x$  are of interest as hard, wide band-gap materials and also as excellent protective coatings when prepared with a cubic crystal structure or even in the amorphous state with predominantly  $\text{sp}^3$  bonding. The deposition of these materials via PECVD has been carried out from mixtures of borazine,  $\text{B}_3\text{N}_3\text{H}_6$ ,  $\text{C}_2\text{H}_2$ , and  $\text{N}_2$ . The optical energy gaps of the films have been found to be larger when  $\text{N}_2$  is added to the plasma, probably as a result of the removal of B-B bonds which absorb at lower energies than B-N bonds.

2. completion of the studies of the initial growth phase of CVD diamond films.

The critical initial phase of the CVD of diamond films in an ASTeX CVD reactor has been studied via emission spectrometry using a two-color infrared pyrometer. The model for the infrared radiation emitted by the film/substrate system which includes both interference in the film and scattering effects from the rough surface of the growing diamond film has been applied to the analysis of the results. The results obtained indicate that two distinct growth regimes exist: an initial period of rapidly increasing roughness before the diamond nuclei coalesce, followed by a slower increase of roughness with thickness as the continuous diamond film grows further.

The ability to achieve real-time control of the deposition process by this technique should lead to the efficient deposition of diamond films with superior properties.

3. establishment of an experimental facility for the measurement of the thermal conductivity of thin films of semiconductors and insulators.

A commercial thermal conductivity measuring instrument has been purchased from INRAD and has been installed in our laboratory. Initial measurements indicate that this instrument will be very useful for the determination of the thermal conductivities of films of disordered semiconductors and insulators such as a-B:N:H.

#### Accomplishments/New Findings:

1. continuation of the studies of the deposition and characterization of amorphous BN:C alloy films.

It has been found that the optical energy gaps of a-B:N:H films increase when N<sub>2</sub> is added to the plasma, probably as a result of the removal of B-B bonds which absorb at lower energies than B-N bonds.

2. completion of the studies of the initial growth phase of CVD diamond films.

Results have been obtained which indicate that two distinct growth regimes exist: an initial period of rapidly increasing roughness before the diamond nuclei coalesce, followed by a slower increase of roughness with thickness as the continuous diamond film grows further. The ability to achieve real-time control of the deposition process by this technique should lead to the efficient deposition of diamond films with superior properties.

#### List of professional personnel:

Principal investigator: Frederick W. Smith, Professor of Physics

Postdoctoral research associate: Dr. Zinoviy Akkerman

Postdoctoral research associate: Dr. Zhiping Yin

### List of publications:

1. 'The Role of Thermodynamics in Determining the Short Range Order in Amorphous Insulating Films', F.W. Smith, in Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials (SSDM '95).
2. 'Atomic Bonding in Amorphous Carbon Alloys: a Thermodynamic Approach', H. Efstathiadis, Z. Akkerman, and F.W. Smith, J. Appl. Phys. 79, 2954(1996).
3. 'Measurements and Modeling of the Optical Constants for Rough Surface Diamond Thin Films', Z. Yin, H.S. Tan, and F.W. Smith, Mat. Res. Soc. Symp. Proc. 416, 205(1996).
4. 'Thermodynamic Modeling of the Atomic Bonding in Covalent  $C_x(BN)_{1-x}$  Alloys', Z.I. Akkerman, H. Efstathiadis, and F.W. Smith, Mat. Res. Soc. Symp. Proc. ?, ?(1996).
5. "Determination of the Optical Constants of Diamond Films with a Rough Growth Surface", (Z. Yin, H.S. Tan, and F.W. Smith), Diamond and Rel. Mater. 5, 1490(1996).
6. "Optical Properties and Microstructure of CVD Diamond Films", (Z. Yin, Z. Akkerman, B.X. Yang, and F.W. Smith), Diamond and Rel. Mater. 6, 153(1997).
7. "Thermal Stability of Diamondlike Carbon Films", (Z.L. Akkerman, H. Efstathiadis, and F.W. Smith), J. Appl. Phys. 80, 3068(1996).
8. "Determination of Film Growth Rate and Surface Roughness Using In-situ Pyrometry", (Z. Yin, Z.L. Akkerman, F.W. Smith, and R. Gat), in Thin Films - Structure and Morphology, eds. S.C. Moss et al (MRS, vol. 441, 1997, Pittsburgh, PA), p. 653.
9. "In situ Determination of the Surface Roughness of Diamond Films Using Optical pyrometry", (Z.L. Akkerman, Y. Song, Z. Yin, F.W. Smith, and R. Gat), Appl. Phys. Lett. 72, (23 Feb 1998).

### Interactions/Transitions:

- a. Participation/presentations at meetings, conferences, seminars, etc.  
papers presented at the MRS Fall 1997 meeting in Boston:

"In Situ Determination of Surface Roughness from Optical Pyrometric Studies of the Initial Growth of CVD Diamond Films", Z.L. Akkerman, Y. Song, Z. Yin, F.W. Smith, and R. Gat.

"Plasma-enhanced Chemical Vapor Deposition of Covalent BN-C-H Alloys", Z.L. Akkerman and F.W. Smith

b. Collaborations

c. Transitions

#### New Discoveries and Summary of Previous Key results:

1. Two distinct growth regimes have been found to exist for the CVD of diamond films: an initial period of rapidly increasing roughness before the diamond nuclei coalesce, followed by a slower increase of roughness with thickness as the continuous diamond film grows further. The ability to achieve real-time control of the deposition process by this technique should lead to the efficient deposition of diamond films with superior properties.

2. The difficulty in incorporating more than about 10-15 at % N in PECVD  $a\text{-C}_x\text{N}_y\text{H}_z$  films has been shown to be related to etching of the films by the plasma through the formation of stable HCN molecules.

3. Predictions have been made for the bonding in low dielectric constant  $a\text{-SiO}_2\text{:F}$  and  $a\text{-SiO}_2\text{:F:H}$  alloys: Si-O and Si-F bonds are strongly preferred in  $a\text{-SiO}_2\text{:F}$  alloy films while Si-O, Si-F, and O-H bonds are strongly preferred in  $a\text{-SiO}_2\text{:F:H}$  alloy films.

4. A straight-forward experimental procedure has been developed for determining the optical constants along with the volume fraction of the non-diamond carbon component of rough microcrystalline CVD diamond films.

5. The effects of entropy have been found to play a critical role in determining the atomic bonding in diamond-like carbon alloys. The effects of entropy lead to bonding disorder and can explain the appearance of a significant amount of tetrahedral  $sp^3$  diamond-like bonding in these alloy films even under conditions where  $sp^2$  graphitic bonding is expected to dominate on the basis of energy considerations alone.

6. Phase separation into distinct ' $a\text{-Si}_x\text{C}_y$ ' and ' $a\text{-Ge}$ ' regions is predicted to occur in  $a\text{-Si}_x\text{C}_y\text{Ge}_z$  alloys due to the preference for Si-C and Ge-Ge bonds.